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(21) International Application Number: PCT/NL99/00190 (22) International Filing Date: 30 March 1999 (30.03.99) (30) Priority Data: 1008746 30 March 1998 (30.03.98) NL (71) Applicant (for all designated States except US): STICHT- ING ENERGIEONDERZOEK CENTRUM NEDERLAND [NL/NL]; Westerduinweg 3, NL-1755 Le Petten (NL). (72) Inventors; and (75) Inventors/Applicants (for US only): RAK, Zbigniew, Stanis- law [NL/NL]; Vijzelstraat 13, NL-1825 KT Alkmaar (NL). VERHAAK, Michael, Johannes, Franciscus, Maria [NL/NL]; Westerweg 41, NL-1815 DB Alkmaar (NL). BOS, Ariejan [NL/NL]; Zwarte Dolfijn 31, NL-1704 VR Heerhugowaard (NL). CENTI, Gabriele [IT/IT]; Via Verso Lido, 7, I-98165 Ganzirri (IT). (74) Agents: DE BRUIJN, Leendert, C. et al.; Nederlandsch Octrooibureau, Scheveningseweg 82, P.O. Box 29720, NL-2502 LS The Hague (NL).		(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: METHOD FOR THE CONVERSION OF DINITROGEN OXIDE		
(57) Abstract The invention relates to a method for the catalytic reduction of dinitrogen oxide (N ₂ O) in the presence of zeolite with the addition of a reducing agent, characterised in that the reducing agent used is a saturated hydrocarbon such as methane (CH ₄), propane (C ₃ H ₈), LPG (C ₃ H ₈ /C ₄ H ₁₀) or a combination of these reducing agents. It has been found that temperatures of 400 °C or lower can be achieved for complete N ₂ O conversion even with very low concentrations of the reducing agent and in the presence of water vapour.		

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Method for the conversion of dinitrogen oxide

The invention relates to a method for the catalytic reduction of dinitrogen oxide (N_2O) in the presence of a zeolite as catalyst.

5 Dinitrogen oxide (N_2O) is a byproduct in the formation of adipic acid for the production of nylon and in the formation of nitric acid, occurs in the exhaust gases of motor vehicles which have internal combustion engines and is formed in off-gases at high temperature. Because dinitrogen oxide makes a 270 times greater contribution to the greenhouse effect than does carbon dioxide, a reduction in the emissions thereof is urgent
10 from an environmental standpoint and a great deal of research is being carried out in this field.

From Catalysis Letters 44 (1997); J.C. Balzer AG Science Publishers, pages 271-274, it is known to reduce dinitrogen oxide by passing it with propene over a Fe-MFI or Cu-MFI catalyst. With this method the propene concentration is 1000 ppm and the
15 dinitrogen oxide concentration 500 ppm and for the Fe-MFI catalyst a conversion of approximately 75 % is obtained at a temperature of approximately 400 °C and in the presence of water vapour.

From the 11th International Congress on Catalysis-40th anniversary Studies in Surface Science and Catalysis vol. 101 (1996); Elsevier Science B.V., pages 641-650, it is known
20 to decompose N_2O in the presence of a ZSM-5 catalyst such as Cu-, Fe- and Co-substituted ZSM-5 zeolites.

US-A 5 171 553 discloses the decomposition of N_2O to give nitrogen and oxygen by the use of a zeolite of the BETA, MOR, MFI, MEL or FER type which has been at least partially substituted by a metal compound of copper, cobalt, rhodium, iridium, ruthenium
25 or palladium.

US-A 4 571 329 and JP-A 08057262 disclose reduction of N_2O by ammonia using a zeolite substituted by iron. Furthermore, JP-A 09000884 discloses reduction of N_2O with an alcohol and/or a hydrocarbon using a zeolite substituted by iron.

US-A 5 149 512 discloses a method for the catalytic reduction of NO_x (i.e. NO and
30 NO_2) using methane as reducing agent and in the presence of oxygen and a metal-substituted zeolite having a silicon/aluminium ratio greater than 2.5.

From Applied Catalysis B: Environmental, 2 (1993); Elsevier Science Publishers B.V., Amsterdam, pages 239-256, it is known to reduce NO_x by passing it over a Co-, Mn- or Ni-ZSM-5 catalyst in the presence of methane.

Catalysis Today 22 (1994), Elsevier, pages 147-169 gives a review of catalysts and reducing agents for reducing the emission of nitrogen oxides (NO and NO₂), including metal-substituted ZSM-5 type zeolites and other zeolites in combination with methane, propane, propene and the like.

5 One aim of the present invention is to provide a method for the reduction of dinitrogen oxide at relatively low temperatures, with the conversion efficiency having a relatively low sensitivity to the presence of water (H₂O), oxygen (O₂), carbon monoxide (CO) and sulphur dioxide (concentrations below 200 ppm SO₂).

A further aim of the present invention is to provide a catalyst which has a high
10 chemical and thermal stability in the presence of the said gas components.

To this end the invention is characterised in that a saturated hydrocarbon, preferably methane (CH₄), propane (C₃H₈) or LPG (mixture of C₃H₈ and C₄H₁₀), or a combination thereof, is used as reducing agent.

It has been found, surprisingly, that by using a saturated hydrocarbon, such as
15 methane, propane or LPG, as reducing agent the reduction in the presence of a zeolite catalyst can be carried out at temperatures below 400 °C and the sensitivity of the conversion is only slightly adversely affected by the presence of water. Furthermore, methane and propane are inexpensive raw materials, certainly compared with propene as described in Catalysis Letters 44 (1997), and the costs of the conversion consequently
20 remain restricted. In particular, it has been found that an iron-substituted zeolite in the presence of methane and propane gives better conversion than other metal-substituted zeolites. Preferably, an Fe-ZSM-5 type zeolite is used as catalyst without the addition of expensive noble metals. Efficient conversion takes place at an SiO₂:Al₂O₃ ratio of less than 100, preferably of less than 65, and most preferentially of less than 40. A further advantage
25 compared with the prior art is that the preparation of the Fe-ZSM-5 catalysts is technically simple. The iron-substituted zeolites display high stability as a function of time in the presence of gas components such as H₂O, O₂, CO, NH₃ and SO₂.

The invention will be explained in more detail with the aid of the following examples together with the appended figures.

30 In the figures:

Figure 1 shows the conversion activity of a catalyst D for N₂O without reducing agent in the absence and the presence of 2 % water,

Figure 2 shows the conversion activity of a catalyst D in the presence of 1500, 1000,

500 or 230 ppm C_3H_8 in addition to 6 % oxygen and 2 % water,

Figure 3 shows the stability of the N_2O conversion with catalyst D in the presence of 6 % O_2 , 2 % H_2O and 1500 ppm C_3H_8 at 340 °C.

Figure 4 shows the effect of water on the stability of catalyst D in the presence of
5 6 % O_2 and 125 ppm CH_4 at 360 °C.

In the following tests Fe-ZSM-5 catalysts have been prepared from Mohr's salts by means of ion exchange. The conversion of N_2O to N_2 and O_2 and the influence of 2 % water on the conversion has then been determined in III below. The effect of the reducing agent and the effect of the concentration thereof have also been determined in, respectively,
10 IV and V. The stability of the catalyst and the effect of the $SiO_2:Al_2O_3$ ratio have been given in VI and VII below. The effect of ammonia on the catalytic reduction with and without methane has been determined in VIII.

I. Preparation of Fe-ZSM-5 catalysts

15

The catalysts according to the present invention were produced by adding ZSM-5 powder (dried for 24 hours at 125 °C) to a solution of $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$ (Mohr's salt). The ion exchange conditions are indicated in Table 1.

Table 1

Ion exchange conditions			
Catalyst	Powder	Solution	Parameters
5	A	10 g	1 litre
	NH ₄ ZSM5-27	0.01M Fe	1x8 h in N ₂ atm at 80 °C
10	B	10 g	1 litre
	NH ₄ ZSM5-27	0.01M Fe	2x8 h in N ₂ atm at 80 °C
15	C	10 g	1 litre
	NH ₄ ZSM5-27	0.01M Fe	1x8 h at 80 °C
20	D	10 g	1 litre
	NH ₄ ZSM5-27	0.01M Fe	2x8 h at 80 °C
25	E	10 g	1 litre
	NH ₄ ZSM5-55	0.01M Fe	1x8 h at 80 °C

Following the ion exchange step, the suspensions were filtered through a Buchner funnel containing a strip of filter paper. If a second ion exchange step was carried out, the filter cake was left to stand overnight on the filter paper. In other cases the filter cake was introduced into 1 litre demineralised water and stirred for half an hour and then filtered off. The pulverulent catalysts were dried at 80 °C for 16 hours and then calcined at 550 °C for 5 hours.

II. Test equipment

The conversion of dinitrogen oxide (N_2O) was studied in an automated micro-flow set-up, operating under atmospheric pressure. The following gases are available to the set-up: He (optionally with H_2O), NH_3 , H_2 , O_2 , N_2 , CO , CO_2 and CH_4 . The gases O_2 , N_2 , CO_2 and CH_4 were determined with the aid of a Varian gas chromatograph model 3300, equipped with a methaniser, a TCD detector and a FID detector. N_2O and CO were determined using a Bomem FT infrared analyser model MB 100. The precursor was contained in a reactor made of pyrex glass having an internal diameter of 10 mm. The catalyst bed was covered with glass wool and a layer of glass beads. The height of the catalyst bed was 10 mm, whilst the gas flow was approximately 150 ml/min. The space velocity (SV) in this case was $11\,500\text{ h}^{-1}$. The requisite amount of precursor (0.5 - 0.71 mm fraction) was approximately 500 mg. The temperature was measured immediately below the catalyst bed with the aid of a Cr/Al thermocouple. During the tests 10 % and 1 % C_3H_8 , 4 % CH_4 and/or 0.5 % NH_3 in helium as carrier gas were mixed with 0.2 % N_2O in helium and 10 % O_2 in helium. Prior to the conversion reaction of N_2O , the catalyst samples were flushed with helium for 15 minutes at 20 °C. In a mixture of 10 % O_2 in helium, the temperature was raised to 500 °C, the catalyst being kept at this temperature for two hours to remove adsorbed elements. The sample was cooled in helium to the initial temperature of the test and was exposed at this temperature for two hours to the reactants feed in order to prevent adsorption effects.

The general test conditions for the N_2O reduction tests are given in Table 2.

Quantitative determinations of the N_2O , C_3H_8 , CH_4 and NH_3 concentrations were carried out by means of infrared analysis. When CO was present in the tested gas, the N_2O signals were corrected since the entire N_2O absorption band ($2143\text{-}2222\text{ cm}^{-1}$) is coincident with the CO absorption band ($1970\text{-}2222\text{ cm}^{-1}$). The contribution of CO to the N_2O band was calculated by extrapolation of the measured free portion of the CO band (that is to say $1970\text{-}2143\text{ cm}^{-1}$). The extrapolation was based on previous measurements on pure CO . The deduction of the CO contribution from the values measured in the $2143\text{-}2222\text{ cm}^{-1}$ band gives the corrected N_2O signal. The quantity of CO formed was less than 0.01 % for all determinations.

The conversion values for N_2O , C_3H_8 , CH_4 and NH_3 are based on the infrared signals at 200 °C, that is to say the infrared signal of N_2O , C_3H_8 , CH_4 and NH_3 in the feed, since

there is still no conversion at this temperature. Signals somewhat below zero were measured after complete conversion of N_2O , C_3H_8 , CH_4 or NH_3 had been achieved, and this was probably caused by small fluctuations in the background values and/or in the CO correction values. These small negative signal values resulted in conversion values of above 100 % (up to a maximum of 105 %). Therefore, the temperature at which there was no further increase in the conversion value was taken as $T_{(100\%)}$, that is to say the temperature of complete conversion. The $T_{(50\%)}$ is the temperature at which 50 % of the ingoing N_2O is converted under the conditions as specified in Table 2.

Table 2. General test conditions

Weight of the catalyst sample	500 mg
Particle size	0.50-0.71 mm
Gas flow rate	150 ml/min
Spatial velocity of the gas per hour (GHSV)	approximately 11 500 h^{-1}
Feed	500 ppm N_2O , 6 % O_2 , 2 % H_2O , 250 ppm - 1 % C_3H_8 or 125 ppm - 3 % CH_4 and/or 160 ppm - 500 ppm NH_3 with helium as the balance.
Total pressure	atmospheric
Bed temperature	200 °C → 500 °C → 200 °C (in 20 °C steps every 15 min)

III. Conversion of N_2O without reducing agent

The test results of N_2O conversion with and without 2 % water over Fe-ZSM-5 catalysts A to D are given in Table 3.

It can be seen that the production of the catalysts in an N_2 atmosphere (A and B) instead of in air (C and D) has no influence on the N_2O conversion. An increase in the number of ion exchange steps from 1 to 2 results in a 10 to 20 °C shift towards lower

temperatures in the N_2O conversion plots. The temperature for complete conversion, $T_{(100\%)}$, was approximately 475 °C (without water).

Figure 1 shows the conversion plots for the catalyst D in the absence of reducing agent with and without 2 % water. The presence of 2 % water shifts the $T_{(100\%)}$ to temperatures well above 500 °C. The hysteresis pattern, the non-coincidence of the upward and downward plots, is a characteristic property of the catalyst which is observed if no water is added.

Table 3

10	Catalyst	N_2O $T_{(50\%)}$ (°C)	H_2O conc. (%)
	A	440	0
	B	430	0
	B	485	2
	C	440	0
15	D	425	0
	D	465	2

IV. Conversion of N_2O with propane, methane and carbon monoxide

Figure 2 shows the effect of the reducing agent C_3H_8 that was added in concentrations of 1500, 1000, 500 and 230 ppm to the N_2O using catalyst D. The increase in the conversion activity is striking: 1500 ppm C_3H_8 lowers the $T_{(100\%)}$ for N_2O in the presence of water from well above 500 °C to about 380 °C.

Tests have shown that the addition of CH_4 increased the conversion to virtually the same extent as C_3H_8 , $T_{(100\%)}$ being 400 °C with 3900 ppm CO .

Tests have also shown that the widely tested Cu- and Co-substituted ZSM-5 catalysts, which perform well in the decomposition of N_2O , perform poorly in the conversion of N_2O with propane or methane. The test results for N_2O conversion with 2 % water, 6 % O_2 and 1500 ppm C_3H_8 over Fe-ZSM-5 catalyst D, Cu-ZSM-5 and Co-ZSM-5 are shown in Table

Table 4

Catalyst	N ₂ O T _(50%) (°C)	C ₃ H ₈ T _(100%) (°C)
D	325	420
Cu-ZSM-5	425	360
5 Co-ZSM-5	430	480

The presence of carbon monoxide had a beneficial effect on the N₂O conversion over catalyst D. The T_(100%) reaction temperature was lowered from > 500 °C to 460 and 480 °C with a CO concentration of, respectively, 980 and 500 ppm (including 6 % O₂ and 2 %
 10 H₂O).

V. Effect of the concentration of the reducing agents propane and methane

Various concentrations of C₃H₈ and CH₄ were tested in the conversion of N₂O with
 15 catalyst D, the results of which tests are given in Table 5. The table shows that the addition of more hydrocarbon relative to N₂O (i.e. with an increasing hydrocarbon/N₂O ratio) the temperature at which 50 % N₂O conversion takes place is reduced. Further increase in the propane concentration from 1500 to 10 000 ppm (1 % V/V) gave a further limited improvement in the conversion activity.

20

Table 5

Hydrocarbon conc. (ppm)	N ₂ O T _(50%) (°C)	Hydrocarbon T _(100%) (°C)
C ₃ H ₈ : 1500	325	380
1000	330	360
25 500	340	360
230	350	320
CH ₄ : 3900	360	500 T _(26%)
1900	360	500 T _(34%)
900	365	500 T _(45%)
30 250	380	500 T _(75%)
125	415	440

VI. Stability of the conversion

Catalyst D was tested for stability of the N_2O conversion in the presence of 1500 ppm C_3H_8 for 40 hours at 340 °C. The test results are shown in Figure 3. It can be seen from this figure that no significant decrease in the N_2O conversion takes place.

The presence of 200 ppm SO_2 gave rise to a moderate change in the N_2O conversion. No direct deactivation of the catalyst was observed on the addition of 160 ppm SO_2 .

Catalyst D was also tested in the N_2O conversion in the presence of 125 ppm CH_4 for 65 hours at 360 °C. During this stability test there was alternating addition of 2 % water for periods of 5 hours. The test results which are shown in Figure 4 show that reversible deactivation by water takes place in the period tested.

VII. Effect of the $SiO_2:Al_2O_3$ ratio

Table 6 shows the results of the experiments in which 500 ppm N_2O was reduced in the presence of 1500 ppm C_3H_8 , 2 % H_2O and 6 % O_2 with catalyst C and E, that is to say containing a ZSM-5 zeolite having an $SiO_2:Al_2O_3$ ratio of, respectively, 27 and 55, both monosubstituted by Mohr's salt.

Table 6

Catalyst	N_2O $T_{(50\%)} (°C)$	C_3H_8 $T_{(100\%)} (°C)$
C	325	420
E	345	500 $T_{(96\%)}$

It can be seen that the lower $SiO_2:Al_2O_3$ ratio of 27 resulted in an approximately 20 °C lower conversion temperature than that for the catalyst with an $SiO_2:Al_2O_3$ ratio of 55.

VIII. Conversion of N_2O with ammonia

Table 7 shows the results of the conversion of N_2O with 500 and 160 ppm NH_3 over catalyst D in the presence of 2 % H_2O and 6 % O_2 . It can be seen from Table 6 that ammonia is completely converted over the entire temperature range. The addition of

125 ppm CH₄ to 160 ppm NH₃ results in an additional lowering of the conversion temperature by 45 °C compared with reduction with NH₃ alone.

Table 7

5	-----		
	NH ₃ (ppm)	N ₂ O T _(50%) (°C)	NH ₃ T _(100%) (°C)
	500	395	100
	160	435	100
	160 (+125 ppm CH ₄)	390	<200 (CH ₄ : 500)
	160 (+500 ppm C ₃ H ₈)	340	340 (C ₃ H ₈ : 340)

10

A stability test on catalyst D for 60 hours at 360 °C using 160 ppm NH₃ as reducing agent shows a degree of conversion of N₂O rising from 17 to 20 %. This means that ammonia also does not have an adverse effect on the stability of the catalyst.

Claims

1. Method for the catalytic reduction of dinitrogen oxide (N_2O) in the presence of a zeolite as catalyst with the addition of a reducing agent, characterised in that the reducing agent used is a saturated hydrocarbon ($\text{C}_n\text{H}_{2n+2}$).
5
2. Method according to Claim 1 characterised in that the hydrocarbon reducing agent used is methane (CH_4), propane (C_3H_8) or LPG ($\text{C}_3\text{H}_8/\text{C}_4\text{H}_{10}$) or a combination thereof.
- 10 3. Method according to Claim 1 or 2, characterised in that the concentration of the added hydrocarbon reducing agent is between 100 and 10 000 ppm for 500 ppm N_2O , in other words a molar hydrocarbon/ N_2O ratio of 0.2 to 20 is used.
4. Method according to one of the preceding claims, characterised in that the catalyst
15 comprises a transition metal-substituted zeolite, preferably a zeolite substituted by iron (Fe).
5. Method according to Claim 5, characterised in that the zeolite is ZSM-5.
6. Method according to one of the preceding claims, characterised in that the $\text{SiO}_2:\text{Al}_2\text{O}_3$
20 ratio of the zeolite is less than 100, preferably less than 65 and more preferentially less than/equal to 40.
7. Method according to Claim 5 or 6, characterised in that the zeolite is at least partially substituted by $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$.
25
8. Method according to one of the preceding claims, characterised in that the reduction takes place at a temperature of below 450°C , preferably of below 400°C and more preferentially of below 350°C .

1/2

Fig 1

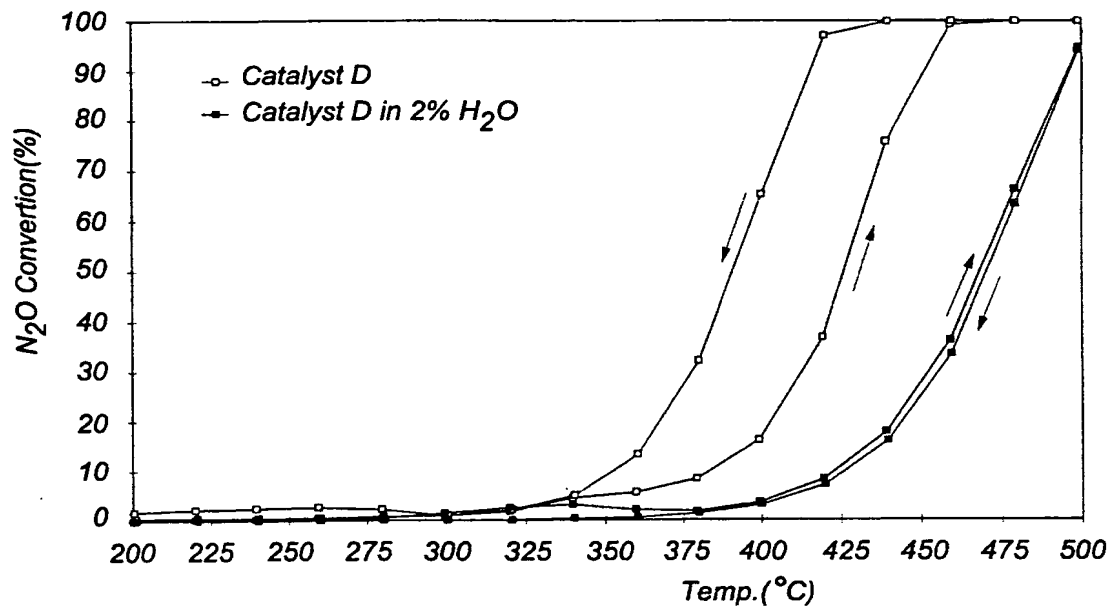


Fig 2

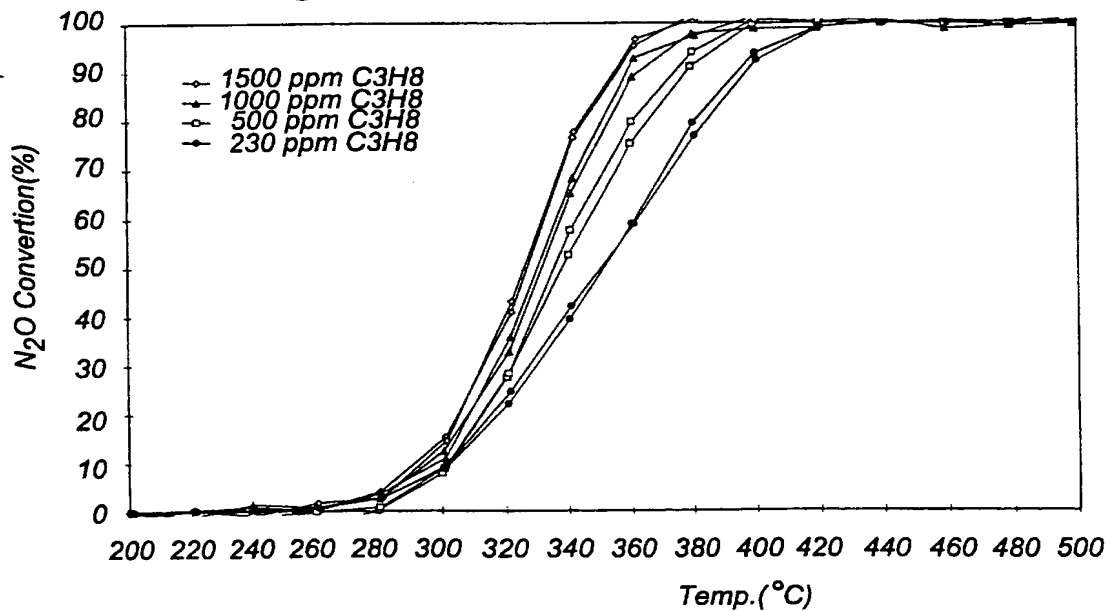


Fig 3

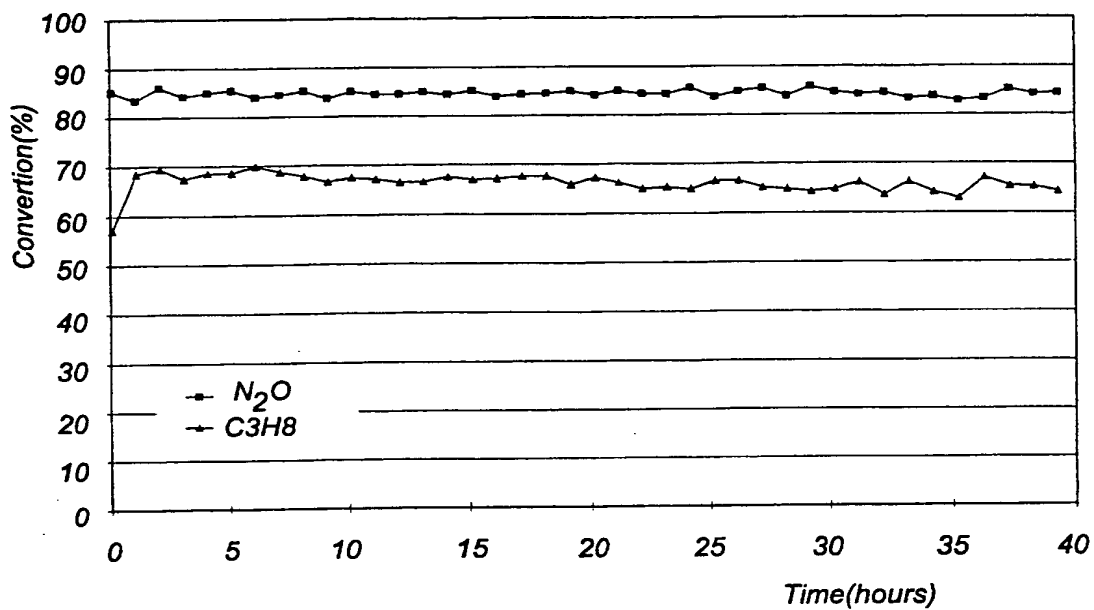
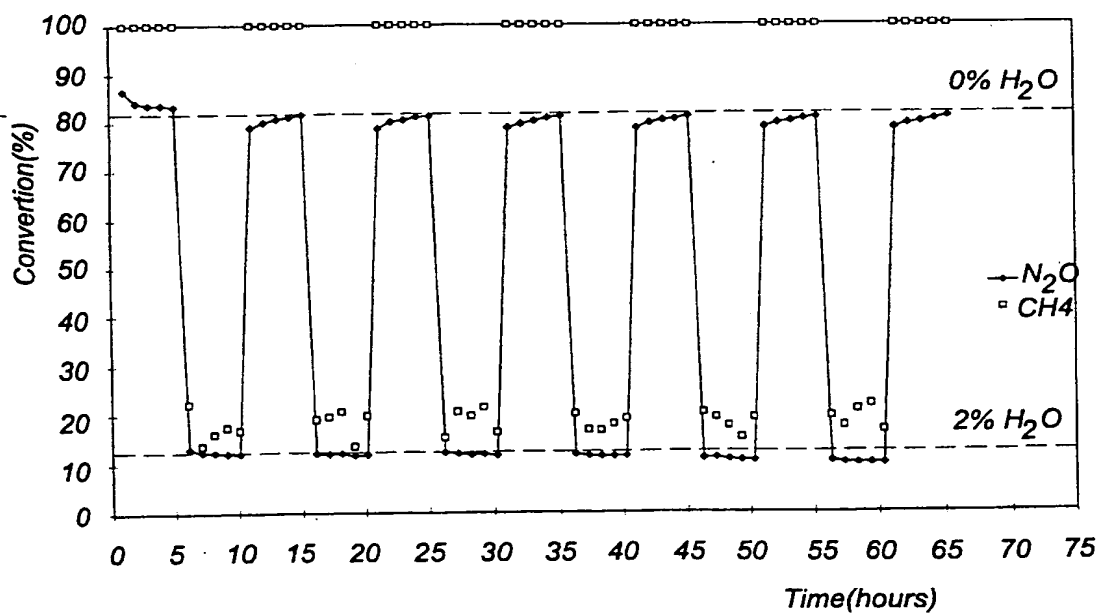


Fig 4



INTERNATIONAL SEARCH REPORT

Internat Application No
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A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 B01D53/86 B01D53/94

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols):
IPC 6 B01D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 524 432 A (JAMES G. HANSEL) 11 June 1996 see column 9, line 54 - column 13, line 3 ---	1-6, 8
X	US 5 149 512 A (YUEJIN LI ET AL.) 22 September 1992 cited in the application see column 4, line 21 - column 8, line 54 -----	1-6, 8

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT

Information on patent family members

Internal Application No

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